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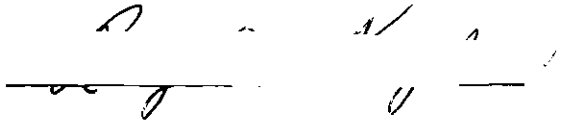

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A STUDY OF THE PRODUCTS FORMED BY THE REACTION OF DIVALENT METAL β-DICARBONYL COMPOUNDS WITH THE METHOXIDE ION

A THESIS

Presented to

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by

Roy Irving Kaplan

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A STUDY OF THE PRODUCTS FORMED BY THE REACTION OF DIVALENT METAL β-DICARBONYL COMPOUNDS WITH THE METHOXIDE ION

Approved:

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TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF ILLUSTRATIONS

GLOSSARY OF TERMS

A	acetylacetonate
B.M.	Bohr Magneton
ε	molar extinction coefficient
F	formal concentration
HA	acetylacetone, 2,4-pentanedione
HFA	hexafluoroacetylacetonate
L	orbital angular momentum
λ,max.	maximum wavelength absorption
M	metal ion
μeff.	effective magnetic moment
S	spin angular momentum
Sal	salicylaldehyde
TFA	trifluoroacetylacetonate
χ_g	gram susceptibility
χ_M	molar susceptibility
$\chi_M^{Corr.}$	molar susceptibility corrected for diamagnetism

SUMMARY

The products resulting from the reactions of copper(II), cobalt (II), nickel(II), and magnesium(II) acetylacetonates with the methoxide ion have been studied.

Potentiometric titrations of the parent divalent metal acetylacetonates with potassium hydroxide to form the methoxo derivatives are reversible as are the titrations of the methoxo derivatives with hydrochloric acid.

Magnetic moment studies have shown that the cobalt(II), nickel(II), and magnesium(II) methoxoacetylacetonates have the expected moments, while the copper(II) analog exhibits a moment considerably below that expected for a d^9 case. Either a short copper-copper bond or the superexchange phenomenon can account for this observation.

The molecular associations range from four to eight in all the methoxo complexes except the copper(II). Its dimeric structure at several concentrations in chloroform seems to indicate a definite stability at that association number.

The infrared spectra of the methoxo complexes show absorption bands which are much sharper than those bands observed for the parent acetylacetonates. These spectra seem to indicate that while all the methoxo derivatives have bridging methoxide groups, the nickel complex also has terminal methoxides. There is no significant change in the bonding of the acetylacetonate group when the parent acetylacetonates are converted to their corresponding methoxo derivatives. The cobalt(II)

and nickel(II) derivatives exhibit visible spectra indicating octahedrally coordinated complexes, while the copper(II) complex is probably square-planar with bridging methoxide groups.

CHAPTER I

INTRODUCTION AND HISTORICAL BACKGROUND

Metal chelates of β-dicarbonyl compounds have undergone extensive study in recent years. These complexes are generally easy to prepare, stable under normal working conditions, and formed by a variety of transitional and non-transitional metals. To fully understand the physical and chemical properties of the methoxo derivatives of these metal chelates, it will be profitable to first examine the properties of their parent compounds and their metal ions in general.

Magnetic Properties of Octahedral Cobalt(II) and Nickel(II)

Perhaps the first transition element series has received the greatest amount of attention in the recent literature because of the magnetic behavior exhibited by the sets of "3d" electrons (1). Van Vleck (2) has stated that the spin-orbit coupling constants should not be large, and the magnetic moments determined experimentally should be the result of a partial quenching of the orbital angular momentum of the free ion by the ligand fields to which the ion is subject. The moment, then, should range from a value of $\sqrt{4S(S+1)\pm L(L+1)}$ when the orbital contribution is considered to a value of $\sqrt{4S(S+1)}$ when only spin is considered. The experimentally found results, therefore, are a function of how efficiently the orbital angular momentum is quenched.

Although octahedrally coordinated cobalt(II) usually has three unpaired electrons, there are complexes such as $[Co(NO_2)_6]^{4-}$ and

$[Co(diarsine)_3]^{2+}$ in which the cobalt is known to have one unpaired electron (3). High spin octahedral cobalt(II) complexes have magnetic moments which range from 4.7 to 5.2 B.M. Since the spin-only value for three unpaired electrons is 3.89 B.M., the high values may be attributed to a large orbital contribution. Low-spin octahedral cobaltous complexes, although they are relatively rare, show magnetic moments only a little above the spin-only value of 1.8 to 2.0 B.M.

Both $Co(o\text{-phenanthroline})_3(ClO_4)_2$ (5) and $K[CoA_3]$ have "octahedrally" coordinated cobalt atoms. The stereochemistry of the latter complex shows slight deviations from perfect symmetry because the ligand is bidentate, and the ions outside the coordination sphere have a great influence on the packing of the lattice (4).

A table of the magnetic data of these compounds is given below.

Table 1. Magnetic Data for Illustrative Cobalt(II) Complexes

Complex	Diamagnetic Corrections x 10^6	μeff., 90°	μeff., 300°
$(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$	184	4.53	4.90
$Co(o\text{-phen})_3(ClO_4)_2$	394	5.54	4.70
$K(CoA_3)$	192	5.02	4.70

Octahedral nickel(II) complexes show relatively simple magnetic behavior. From a simple "d"-orbital splitting diagram and the energy

level diagram, it may be observed that octahedral cases have two unpaired electrons, and the magnetic moments lie between 2.9 and 3.4 B.M. (3). An obvious exception to this rule is the complex Ni[o-phenylbis (dimethylarsine)]$_3^{2+}$ which is diamagnetic. It is possible, however, for nickel(II) complexes to be either diamagnetic or have two unpaired electrons depending upon whether the energy separation of the uppermost "d" orbitals is greater or less than the energy necessary to cause electron pairing.

Cotton and Fackler (6) have reported a magnetic moment of 3.27 B.M. for the octahedrally coordinated nickel(II) acetylacetonate trimer, whose structure appears in the section on molecular association. Other complexes reported in the same paper include the nickelous complexes of diisobutyrylmethane and dipivaloylmethane. The latter complex showed a diamagnetic character at room temperature because of its planarity.

Subnormal Magnetic Moments in Copper(II) Compounds

The copper(II) ion is a "$3d^9$" case, and it is to be expected that it should have a magnetic moment for a spin-only value of about 1.73 B.M. Indeed, most copper(II) compounds do exhibit moments between 1.72 and 2.20 B.M. However, as early as 1915 Lifschitz and Rosenbohm (7) recognized an abnormally low magnetic moment of about 1.4 B.M. for copper(II) acetate monohydrate.

Most dimeric copper(II) compounds with subnormal magnetic moments can be roughly grouped into two distinct classes, based on the type of magnetic interaction mechanism (8). Presently, the two generally accepted mechanisms are (a) direct copper-copper interaction, when the copper ions are close together, and (b) super-exchange, when the intermetallic distance is too long for direct interaction.

The primary contributing factors to direct interaction include, of course, copper-copper distance, and the nature of the attached ligand. In superexchange the space between neighboring copper ions is occupied by one or more bridging diamagnetic atoms. Three predominant factors must be considered in finding a pathway of lowest energy for migration of the unpaired "3d" electron via these diamagnetic atoms: (a) relative energies of the alternate paths, (b) "transmission probability" associated with each path, which is roughly proportional to the overlap between copper and ligands, and (c) relative energies of the ground and excited states of the copper under the influence of the ligand.

Copper(II) acetate monohydrate is representative of the direct metal-metal interaction class. The X-ray structure analysis of this compound has shown that the intermetallic distance in the dimer is 2.64 A , only 0.08 A longer than the interatomic distance in metallic copper (9). Most of the compounds in the superexchange class contain a bridging oxygen atom joining the two copper ions. An example of this class, whose structure was recently completed, is the (pyridine N-oxide)-copper(II)chloride dimer (10). Its subnormal magnetic moment of only 0.85 B.M. at room temperature had suggested that the complex had a bridged structure with strong metal-metal interaction. It was found that the oxygens of the pyridine oxide do indeed bridge, but that the intermetallic distance was 3.23 A. This distance is considerably longer than that observed for most dimeric copper systems whose low magnetic moments are due to direct metallic interaction.

Molecular Association in the Divalent Metal Acetylacetonates

A knowledge of the molecular association involved in the metal acetylacetonates has been recognized for some time as a key to a thorough understanding of the chemistry of these chelates.

Copper(II) acetylacetonate was one of the first of the series studied (11). Cox and Webster found that the crystal structure was probably monoclinc with two molecules per unit cell. Their work, based on space group considerations, cell dimensions, and optical properties, indicated that the molecule was planar. In 1953, a two-dimensional projection of the electron density was published (12) which definitely showed the complex to be planar. Dahl's work (13) on the structure was a three-dimensional X-ray structure analysis showing the molecule to be symmetrical with respect to a plane bisecting the two central methylene carbons and the central copper atom. This would be expected and required by the enolate resonance.

Cotton and Soderberg (14) determined, through spectroscopic studies and molecular weight measurements, that cobalt(II) acetylacetonate in non-coordinating solvents such as benzene or cyclohexane was present as dimers, trimers, and even higher polymers. An apparent leveling off of the association number at two in high concentrations of carbon tetrachloride at 77° may be due to the authentic stability of a dimeric specie, or it may indicate the presence of coordinating impurities such as water, alcohols, or ethers. The impurities are known to split high weight polymers into units in which the cobalt is octahedrally coordinated. A spectral comparison of the cobalt acetylacetonate monomer with known tetrahedral cobalt complexes indicates that the monomeric structure is tetrahedral in solution.

The complete single crystal X-ray structure determination of anhydrous cobalt(II) acetylacetonate was reported in 1964 (15). A schematic diagram of the structure is shown in Figure 1.. The complex is a centrosymmetric tetramer which contains three distinct types of rings: those with both oxygens serving as bridges, those with one oxygen serving as a bridge between two cobalt atoms, and those with both oxygens bonded to only one cobalt atom.

Shibata's X-ray powder patterns (16) erroneously indicated that nickel(II) acetylacetonate has a tetrahedral configuration in agreement with Linus Pauling's presumptions. However, previous work (17) employing electron diffraction techniques had shown the gaseous chelate to have a planar configuration. The assumption was made that the configuration changed with temperature, due to the small energy difference between the two configurations.

Single crystal X-ray work has verified that anhydrous nickel(II) acetylacetonate contains trimeric molecules (18). After publication of the structure, ebullioscopic molecular weight determinations in benzene and carbon tetrachloride were published which confirmed the association values of approximately three (18). Mason and Pauling (19) have recently deduced the complete structure from data obtained earlier by Bullen (20). The nickel atoms are connected together in symmetrical, linear chains of three, and each nickel atom is surrounded by a distorted octahedron of oxygen atoms in much the same manner as the cobalt analog. The schematic structure of the complex is shown in Figure 2.

It is interesting to note that if the methyl groups are replaced by tert-butyl groups in the nickel acetylacetonate, steric hindrance

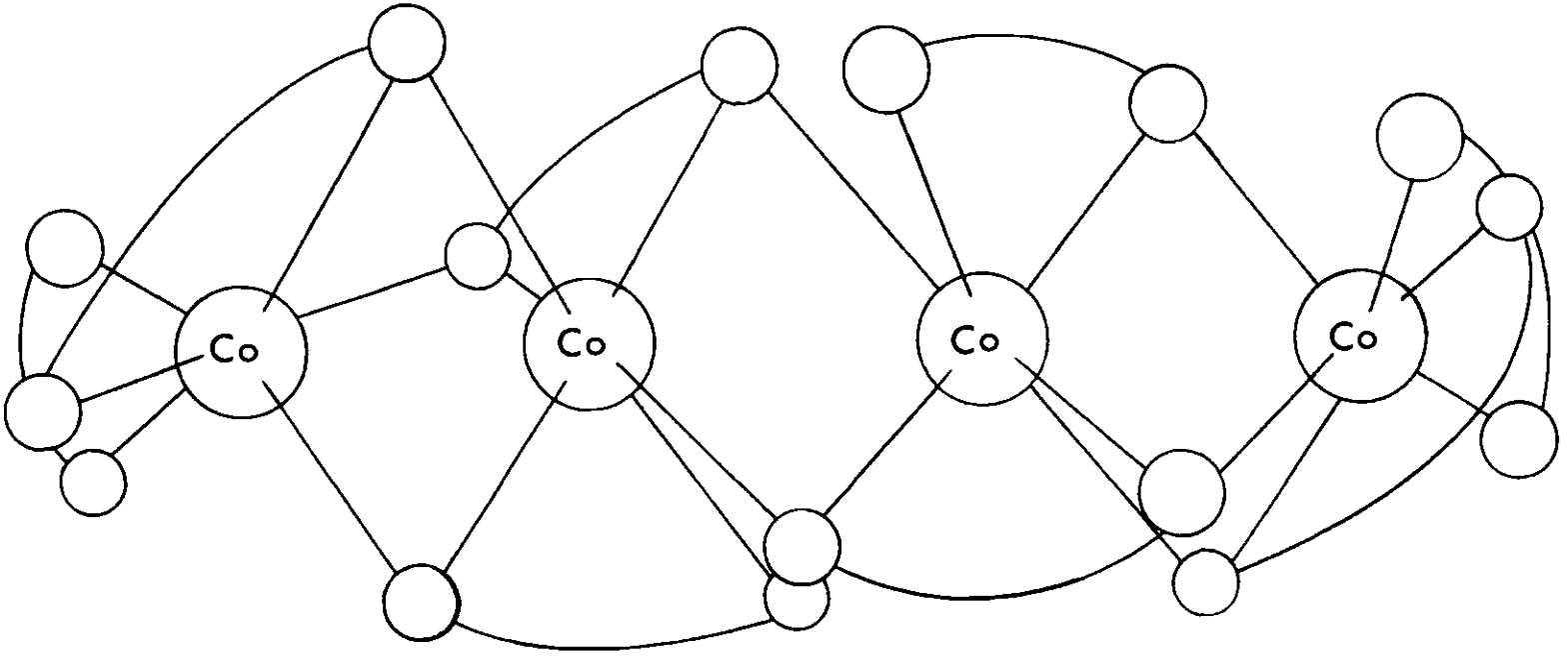


Figure 1. The Schematic Diagram of the Structure of the Cobalt(II) Acetylacetonate Tetramer.

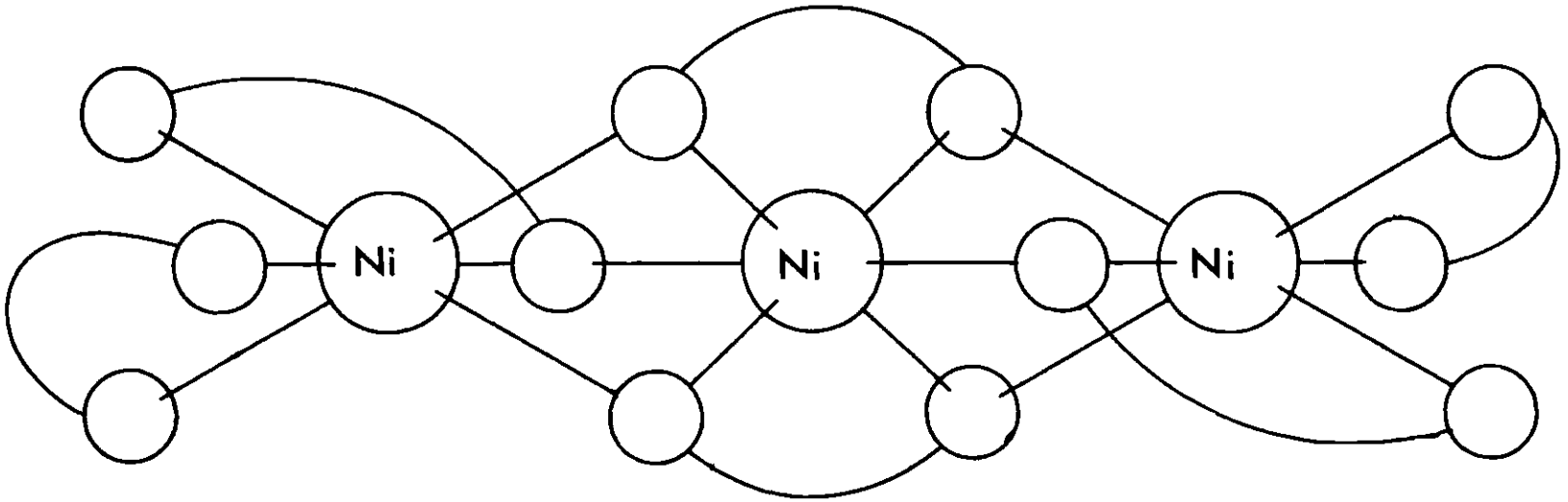
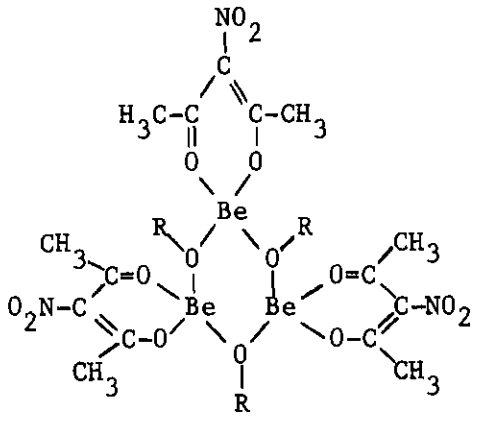


Figure 2. The Schematic Diagram of the Structure of the Nickel(II) Acetylacetonate Trimer.

completely prevents trimer formation and the complex behaves as a spin-paired planar nickel(II) complex (18). However, if the methyl groups are replaced by isopropyl groups, the complex shows partial, reversible and temperature-dependent association between 0° and 60°. Nickel(II) acetylacetonate, itself, dissociates reversibly into monomers at temperatures around 200°.

Many complexes containing bridging alkoxide groups have been studied by workers in recent years (21). Wentworth and Brubaker (22) reported diamagnetic niobium complexes with methoxo and ethoxo groups which suggest polymerization. The infrared spectra of these complexes lead to the conclusion that the alkoxide groups are bridging.

Klein and Bailar (23) have recently reported that the nitration of beryllium acetylacetonate in a beryllium nitrate-acetic anhydride reagent produced a hydroxide complex. If this complex were refluxed in methanol a methoxide precipitated, or an ethoxide precipitated if the hydroxide complex were refluxed in ethanol. These complexes were characterized by elemental analysis, infrared spectra, and molecular weight measurements. Although both dimers and trimers are possible from the spectral and elemental analysis data, high molecular weight values indicate a trimeric association with the following suggested structure.



R = H, CH_3, CH_3CH_2

Vibrational and Electronic Spectra of Divalent Metal Acetylacetonate Complexes

The vibrational and electronic spectra of the acetylacetonates are valuable tools by which the chemistry and structure of these complexes have been elucidated in recent years. The infrared spectrum of acetylacetone itself shows several important features (24): (a) no absorption in the 7000 cm^{-1} region where overtones of normal hydrogen-bonded hydroxylic groups usually occur. (b) an OH absorption near the 2700 cm^{-1} region, (c) no CO absorption at 1670 cm^{-1} common for a conjugated ketone, and (d) an unusually intense and broad band in the 1640-1530 cm^{-1} region.

Examination of the infrared spectra of the divalent metal acetylacetonates in specific spectral regions shows important relations between the parent acetylacetone and the metal chelate derivatives (25).

(A) 4000-1650 cm^{-1} Region. The OH...O absorption in acetylacetone is completely lacking in the metal chelates, while the symmetric and the antisymmetric CH_3-stretching frequencies remain unchanged. A shift to higher frequencies upon chelation noticed on the methylene carbon-hydrogen stretch is probably due to the change of environment of the

proton from an olefenic one to an aromatic one.

(B) 1650-1200 cm^{-1} Region. An intense, broad band around 1610 cm^{-1}, characteristic of 1,3-diketones, disappears on chelation. The most important chelate band, the perturbed carbonyl band, is usually located about 1580 cm^{-1}. The copper chelates of eleven different β-diketones studied showed a definite shift to lower frequencies from the hydrogen-bonded carbonyl band in the parent β-diketone. There was apparently no relation between the stability of these complexes and the positions of the perturbed carbonyl absorption bands.

It has been pointed out (25) that whereas a phenyl group attached to a carbonyl group in the ligand might establish interfering conjugation through a quinoid-like structure, thereby decreasing the double bond character of the adjacent carbonyl group, decreasing the strength of the carbon-oxygen bond, and lowering the carbonyl band; strong electr-negative groups attached to the chelate ring will have just the opposite effect.

(C) 1500-800 cm^{-1} Region. A band caused by methyl deformation is centered around 1425 cm^{-1} in both the parent acetylacetones and in the metal chelates. Compounds which contain no methyl group in the chelate ring fail to absorb in the 1425 cm^{-1} region.

(D) 800-650 cm^{-1} Region. The strong bands occurring in the upper 700 cm^{-1} region in the 1,3-diketones and their metal chelates are ascribed by Ueno and Martell (26) to be C-H out-of-plane deformation vibrations. The 1,3-diketones which have been substituted at the methylene carbon can have no hydrogen on the carbon-carbon double bond of the ligand enol form or on the carbon-carbon double bond of the metal

chelate; yet when iodo, bromo, or methyl groups are substituted on the methylene carbon bands do appear in the 700 cm^{-1} region, which cannot be caused by hydrogen out-of-plane deformation. Lecompte (27) expects absorption bands due to the metal-oxygen vibrations, below 700 cm^{-1}, but these are absent down to 650 cm^{-1} in most of the β-diketone spectra.

Nakamoto, Morimoto, and Martell (28) have studied the effects of substituents on the infrared spectra of metal acetylacetonates. They assumed, since no structural data were then available for the various substituted compounds, that the bond distances in the chelates do not change appreciably on substitution. They found that the trifluoro- and hexafluoroacetylacetonates of Cu(II) and Ni(II) show shifts in the infrared spectra of the C=C stretch and the C=O stretch to higher frequencies. The stability constants of the trifluoroacetylacetonates are intermediate between those of the acetylacetonato and the hexafluoroacetylacetonato complexes. The CF_3 groups weaken the metal-oxygen bonds, lower stability constants, and strengthen C=C bonds.

Holm and Cotton (29) have reported the ultraviolet spectra of thirty-one metal acetylacetonates in the 240-400 mμ region using chloroform and/or ethanol as solvents. The chelates may be separated into three distinct classes. These are shown in Table 2.

Table 2. Ultraviolet Spectra of Metal Chelates

	Acetylacetonate	Solvent	mμ	λmax., cm^{-1}	ε, (l, $mole^{-1}$, cm^{-1})
Class I	H	$CHCl_3$	274	36,000	10,600
	Li	EtOH	290	34,500	13,000
	Na	EtOH	288	34,700	10,400
Class II	Be	$CHCl_3$	294	34,000	33,300
	Mg	$CHCl_3$	284	35,200	21,200
	Ca	EtOH	290	34,500	25,800
	Sc	$CHCl_3$	297	33,700	28,800
	V	$CHCl_3$	280	35,700	19,600
	Mn(II)	$CHCl_3$	276	36,200	20,500
	Co(II)	$CHCl_3$	292	34,200	16,200
	Ni(II)	$CHCl_3$	265	37,700	15,200
			296	33,800	12,400
Class III	Fe(III)	$CHCl_3$	274	36,500	29,600
	Co(III)	$CHCl_3$	258	38,800	34,000
	Cu(II)	$CHCl_3$	245	40,800	20,100
			296	33,800	24,600

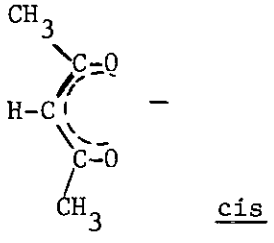
The Class I spectra may be identified by a single, nearly symmetrical peak. Class II spectra exhibit a single, strong band, but a shoulder

always appears on the long wavelength side. The only difference between Class II and Class III spectra is that Class III spectra show a band at higher energy than any band in Class II. Many weaker bands are observed in the 240-400 mμ region, but they are attributed to either charge transfer or ligand field bands.

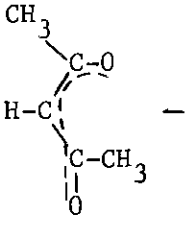
The outstanding feature of each of the three spectral classes, with the exception of Co(III), is the very intense absorption band in the 270-300 mμ region with a maximum molar extinction coefficient usually greater than 20,000. It is thought that a π-π^* type transition accounts for the three bands.

The main absorption band is a sensitive function of several parameters, the most significant of which are cation charge, cation size, and their distortion effects upon the ring π-system and the π-bonding ability of the metal ion.

The alkali metal acetylacetonates are the only chelates in which the electrostatic effect is separable from other effects, expressly the π-bonding factor. Only one peak is evident, although two distinct anion forms are possible, the <u>cis</u> and <u>trans</u> forms.



<u>cis</u>



<u>trans</u>

It must be assumed, therefore, that the anion and the cation are intimately associated in firmly bound ion pairs demanding the <u>cis</u> form of

the diketone.

Metal-oxygen π-bonding, not possible with the alkali metal compounds and extremely unlikely with the alkaline earths, becomes feasible with the transition metals. There is ample evidence that in a conjugated system, as the number of atomic centers over which electrons are delocalized increases, λmax. shifts to longer wavelengths. In transition metal complexes, dπ-pπ bonding increases the length of the π-electron system.

The λmax. decreases proceeding across the first transition series. The two significant changes in the nature of the metal dπ orbitals in this direction are regular drop in energy, which would tend to increase the "d-electron" overlap with the oxygen pπ orbitals, and the steady filling with metal "d" electrons, which would tend to decrease their ability to accept electrons. (29)

No satisfactory explanation can be advanced for the apparent irregularities in the λmax. for the series Sc(III), V(III), Mn(III), Fe(III), Co(III). However, in going from Fe(III) to Co(III), the dπ orbitals become completely filled, thus lessening the delocalization energy.

The shoulder on the long wavelength side of the principal band in the Class II spectra can arise from one of two possibilities: (1) $n-\pi^*$ transitions or (2) singlet-triplet($'\pi-{}^3\pi^*$) transitions. The $n-\pi^*$ transition would involve non-bonding electrons of the ring oxygens moving to anti-bonding MO's of the π-system. Bands of this type have been observed in cyclic systems such as pyridine (30). Cotton and Holm found no direct evidence for the possibility of singlet-triplet transitions of

the π-electrons in the chelate ring system. With the paramagnetic acetylacetonates, with the exception of Cu(II) acetylacetonate, no pronounced shoulder appears on the long wavelength side of the main absorption band, but a number of small bands are present at longer wavelengths.

For the ultraviolet spectra of the metal acetylacetonates there seems to be no simple correlation between λmax. for the most intense absorption and the various characteristic parameters of the metal ions. Such a correlation had been expected since Izatt, Fernelius, and Block (31) showed that when one plots one-half the logarithm of the first plus the second thermodynamic formation constants of the metal ion with the acetylacetonate ion versus the electronegativity of the metal ion, a linear relation results. The stability of these complexes has been shown to be affected by ionic radii of the metal ion and the atomic number.

Spectra of Octahedral Cobalt(II) and Nickel(II)

Jorgensen (32) predicted that octahedral cobalt(II) complexes should exhibit three vibronic bands originating from transitions between the ground state, $^4T_{1g}$, and the three known excited states, $^4T_{2g}$, $^4A_{2g}$, and $^4T_{1g}(P)$, at $\upsilon_1 = 4/5\ (E_1-E_2)\ cm^{-1}$, $\upsilon_2 = 9/5\ (E_1-E_2)\ cm^{-1}$, and $\upsilon_3 = 3/5\ (E_1-E_2) + 15{,}400\ cm^{-1}$. The value for (E_1-E_2) is the energy difference between the two possible levels of a single "d" electron in a cubic crystal field. It was determined that in order to obtain the best possible agreement between observed and calculated absorption data, the following values for the parameter should be assigned: $(E_1-E_2) = 9000\ cm^{-1}$ for $Co(H_2O)_6^{++}$, $(E_1-E_2) = 10{,}500\ cm^{-1}$ for $Co(NH_3)_6^{++}$, and $(E_1-E_2) = 11{,}000\ cm^{-1}$ for $Co(en)_3^{++}$.

The agreement of these assignments with experiment may be seen below in Table 3 (33).

Table 3. Comparison of the Observed and Calculated Absorption Maxima for Cobalt(II) Complexes.

Complex		υ_1	υ_2	υ_3
$Co(H_2O)_6^{++}$	obs.	8,000 cm^{-1}	16,000 cm^{-1}	20,200 cm^{-1}
	calc.	7,200	16,200	20,300
$Co(NH_3)_6^{++}$	obs.	9,000	18,500	21,100
	calc.	8,400	18,900	21,700
$Co(en)_3^{++}$	obs.	9,800	18,700	21,700
	calc.	8,800	19,800	22,000

Spectral studies of $CoSO_4 \cdot 7H_2O$ by Holmes and McClure (34) have shown that the intensities of the bands show a variation with temperature changes, a further indication that the transitions are vibronic in character.

Although complexes of divalent nickel can have varied geometrical configurations, by far the most common is the octahedron (35). Three absorption bands stemming from $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions should be and are, in fact, observed. Jorgensen (36) has reported the spectrum of pale green $Ni(H_2O)_6^{++}$ which has three spin-allowed absorption bands located at 8,500 cm^{-1}, 13,500 cm^{-1}, and 25,300 cm^{-1}. For violet $Ni(NH_3)_6^{++}$ they are found at 10,700 cm^{-1}, 17,500 cm^{-1}, and 28,200 cm^{-1}. These absorption maxima are in good

agreement with the corresponding (E_1-E_2) values in the cobalt(II) complexes. It is noticeable, however, that in a comparison of the spectra of these two complexes the second absorption peak of the hexaaquo complex is double-peaked, whereas the ammine complex shows no such splitting. Jorgensen explains this as a result of the closeness of the $^3T_{1g}(F)$ and the $^1E_g(D)$ states at the Dq value of water. Spin-orbit coupling should then couple the two states, dividing the intensity between them.

CHAPTER 2

PREPARATION OF THE COMPLEXES

Preparation of the Divalent Metal Acetylacetonates

Preparation of the starting compounds, the divalent metal acetylacetonates, consisted simply of mixing 0.25 mole of the metal chloride hydrates dissolved in water with 0.50 mole of 2,4-pentanedione (acetylacetone) dissolved in methanol, addition of 0.50 mole of sodium acetate, and warming gently to insure complete precipitation of the metal chelates (37).

The nickel(II), cobalt(II), and copper(II) acetylacetonates were easily recrystallized by dissolving the chelates in hot methanol, reducing the volume by evaporation, and cooling overnight in a refrigerator. The product obtained from the attempted preparation of the magnesium(II) acetylacetonate by this method was relatively insoluble in either cold or hot methanol. Formation of considerable amounts of magnesium oxide and/or magnesium hydroxyacetylacetonate would probably cause this insolubility. An alternate systhesis of magnesium acetylacetonate, by refluxing magnesium ribbon in excess acetylacetone for four hours, yielded white crystals of the complex upon evaporation of excess acetylacetone and cooling. The complex prepared by this procedure was much more soluble in methanol than the compound formed in the earlier procedure.

These metal chelates were dried using a vacuum desiccator employing concentrated sulfuric acid as the desiccant or by using a drying

pistol heated to 80° for three hours.

Preparation of the Methoxo Derivatives of the Divalent Metal Acetylacetonates

The method of Bertrand and Caine (38) was used to synthesize the methoxo derivatives of the metal acetylacetonates used in this study. A 0.007 mole sample of metal(II) acetylacetonate was dissolved in 350 ml of refluxing methanol, and 0.007 mole of potassium hydroxide in methanol was added dropwise to the refluxing solution over a period of one hour. After two hours at reflux, the solution was filtered while hot. The complexes of nickel(II), cobalt(II), and magnesium(II) had separated from solution as large green, deep red, and white crystals, respectively.

A loss of weight on heating was noted in all cases except the copper(II) complex. Heating at 100° *in vacuo* resulted in the loss of weight equivalent to one mole of methanol per methoxo complex. The cobalt complex changed color from a deep red to a violet.

Therefore, it must be concluded that the nickel(II), cobalt(II), and magnesium(II) methoxo complexes have methanol of solvation, while the copper(II) methoxo complex lacks it.

The copper complex was also different from the other complexes in other ways. It did not separate from solution as large crystals but rather as a violet, microcrystalline solid.

Since it seemed desirable to perform a single crystal X-ray structure determination of the copper complex, an investigation was begun to discover a method of preparing crystals large enough to mount. The use of weaker bases, purer starting materials, varying sublimation temperatures and many recrystallization solvents proved to be futile variations.

The analyses of the above-mentioned and subsequent compounds were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Table 4. Analytical Data for Compounds $MA(CH_3O)(CH_3OH)$

Metal	Calculated		Found	
	Carbon	Hydrogen	Carbon	Hydrogen
Cobalt	38.0	6.3	38.0	5.7
Nickel	38.0	6.3	38.8	5.8
Magnesium	45.5	7.5	45.5	7.8

Table 5. Analytical Data for $CuA(CH_3O)$

Calculated		Found	
Carbon	Hydrogen	Carbon	Hydrogen
37.2	5.6	37.1	5.3

Preparation of Copper(II) Trifluoroacetylacetonate and Copper(II) Hexafluoroacetylacetonate

A 0.09 mole sample of copper nitrate trihydrate was dissolved in 200 ml of water. To this was added with mixing 0.18 mole of the trifluoroacetylacetone /or the hexafluoroacetylacetone dissolved in dry methanol. Immediate precipitation ensued in both cases. The addition of 0.18 mole of sodium acetate in water to each and cooling in an ice

bath completed the precipitation.

The copper(II) trifluoroacetylacetonate thus formed was a bright blue-purple crystalline material. It was recrystallized from dry methanol and dried for two days in a vacuum desiccator over sulfuric acid.

The copper(II) hexafluoroacetylacetonate precipitated from the solution as brilliant emerald green needles. Recrystallization of these needles from dry methanol and drying over sulfuric acid caused a deterioration of the needle structure and a fading of the green color into a dark blue. If the compound were allowed to stand in moist air for a few hours, the green color gradually reappeared.

An alternate procedure for drying the hexafluoroacetylacetonate yielded some interesting results. Drying the complex in a drying pistol over benzene caused immediate sublimation of the green needles. After about an hour all of the green material had sublimed from the sample cup to the cool portion of the pistol leaving behind dark blue crystals. Continued drying of the sample caused the remaining blue solid to migrate from the cup and form a band of blue crystals in the hotter portion of the pistol. After three hours the sublimation was complete and there were two distinct bands observable in the pistol. This unusual behavior seems to indicate that the green complex is a hydrate or possibly a methanolate and the blue complex is the anhydrous material. The volatility of the anhydrous material made elemental analysis difficult.

Table 6. Analytical Data for $Cu(TFA)_2$

Calculated		Found	
Carbon	Hydrogen	Carbon	Hydrogen
32.35	2.16	32.57	2.27

Table 7. Analytical Data for $Cu(HFA)_2$ (Green Portion)

Calculated		Found	
Carbon	Hydrogen	Carbon	Hydrogen
25.05	0.43	24.39	1.01

The actual values found for the carbon and hydrogen in Table 7 fall between those for a monohydrate and a monomethanolate.

Attempted Preparation of the Methoxo Derivatives of $Cu(TFA)_2$ and $Cu(HFA)_2$

It was anticipated that the methoxo derivatives of the trifluoro- and the hexafluoroacetylacetonates could be prepared in the same manner as the other methoxo complexes, but all attempts to do so failed. The electonegativity of the attached fluorines apparently caused a withdrawal of electrons from the ring system and decreased the stability of these complexes. It was impossible to remove only one of the acetylacetonate rings and replace it with the methoxide ion without completely destroying the complex.

Preparation of Bis-(Salicylaldehydato)-copper(II)

A 0.25 mole sample of copper(II) chloride dihydrate dissolved in 200 ml of dry methanol was added to a 0.50 mole sample of salicylaldehyde and warmed. No precipitation resulted until the addition of 0.50 mole of potassium hydroxide in methanol. The dark green precipitate was recrystallized from chloroform. The recrystallized product consisted of thin, green, poorly formed platelets.

Preparation of the Methoxo Derivative of $Cu(Sal)_2$

A 0.005 mole sample of the recrystallized $Cu(Sal)_2$ was dissolved with difficulty in 350 ml of dry methanol. On gradual heating a fluffy, chartreuse precipitate began forming. Addition of a 0.005 mole portion of potassium hydroxide in methanol completed the precipitation. The precipitate was filtered and dried over calcium chloride without further purification.

Table 8. Analytical Data for $Cu(Sal)(CH_3O)$

Calculated		Found	
Carbon	Hydrogen	Carbon	Hydrogen
44.55	3.71	44.49	3.58

Since this methoxo complex is similar to the methoxo complexes of the acetylacetonates, it will not be discussed further in detail.

Preparation of Potassium Acetylacetonate

To a 0.50 mole sample of reagent grade potassium hydroxide in 175 ml of dry, boiling methanol was added a 0.50 mole sample of 2,4-pentanedione (acetylacetone) with stirring. The clear solution immediately became a pale yellow, and cooling to room temperature initiated precipitation of white, crystalline flakes of the product. The crude KA was recrystallized from dry methanol and dried over sulfuric acid in a vacuum desiccator for two days.

CHAPTER 3

EXPERIMENTAL TECHNIQUES AND INSTRUMENTATION

Potentiometric Titrations

Potentiometric titration studies have been used on several previous occasions to examine the stability of divalent metal β-diketones (39), the thermodynamic equilibrium constants of these complexes in mixed solvents (40), and the kinetics of the complex formations (41).

The titrations in this study were run to study the formation aspects of the methoxo complexes. All potentiometric titrations were made using a Beckman Model G pH meter equipped with a Beckman number 40495 glass electrode and a calomel electrode employing a saturated solution of potassium chloride in methanol rather than in water. The use of an alcoholic solution limited the possibility of a precipitation of potassium chloride during the titration process. All measurements were recorded at 27°±1°.

The methanol used as a solvent was dried over magnesium ribbon and distilled. The fraction coming over between 64° and 65° was saved for use. Isopropyl alcohol was distilled, and the fraction boiling between 82° and 84° was collected. Both alcohols were stored in glass stoppered bottles over sodium sulfate.

A magnetic stirrer was utilized to keep any insoluble products formed during the titration suspended.

When the pH scale was used, the instrument was adjusted to a value between 6.00 and 6.25 before the titration was begun. It must be

emphasized that no significance should be placed on the actual values obtained, but only on the "relative" pH values. The millivolt readings are the actual values recorded from the instrument after first "zeroing" it.

A serious problem was encountered when the metal acetylacetonates in isopropyl alcohol were titrated with methanolic potassium hydroxide. Precipitation of the methoxo complexes ensued, and it was difficult to determine the validity of the pH readings. The data, however, were reproducible. When enough base had been added to theoretically complex all of the acetylacetonates with the methoxide ion, the titrations were reversed using hydrochloric acid in isopropyl alcohol. It was noticed that if insufficient time had elapsed between the addition of the aliquot of acid and the time the readings were taken, a shift or hysteresis effect toward the lower millimole end of HCl resulted. This is shown in Figure 3. The two curves gradually merged together if fifteen to twenty minutes were allowed to elapse before the readings were taken. This hysteresis effect was apparently due to the relative insolubility of the methoxo complexes in the alcohols used as solvents and not a real effect due to any irreversibility intrinsic in the reactions.

When the methoxo complexes themselves were the starting materials in the potentiometric titrations and were titrated first with hydrochloric acid and then with potassium hydroxide, the solvent used was N,N-dimethylformamide. The possibility of error due to the precipitation of any products formed was completely eliminated since all products formed were soluble in the solvent throughout the forward and reverse titrations. Poor, if not imperceptible, breaks were evidenced if N,N-dimethylformamide were used as the solvent when the metal

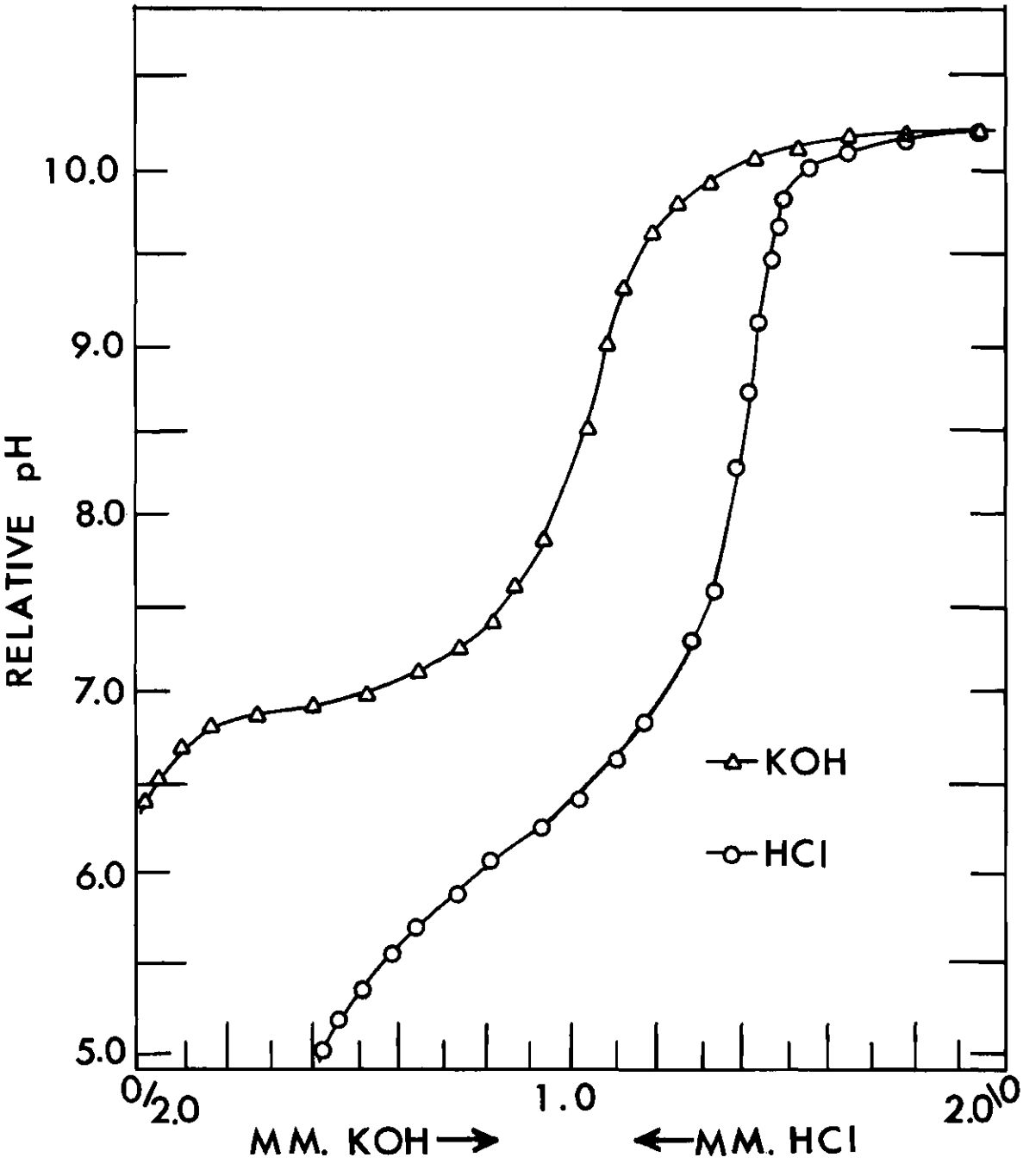


Figure 3. Apparent Hysteresis Effect in the Titration 2.00mm of MA_2.

acetylacetonates were the starting materials.

Magnetic Moment Studies

All of the magnetic moment values were obtained from solid samples. Each sample was finely ground with a mortar and pestle and packed in the sample tubes. The $Hg[Co(CNS)_4]$ complex served as a standard, and it was assigned a susceptibility of 16.44×10^{-6} c.g.s. units.

The Guoy balance used consisted of a Newport Instruments electromagnet equipped with a Mettler Type H 16 microbalance. A glass jacket, which was fitted between the poles of the electromagnet and extended around the sample tube and connecting chain to the base of the balance, limited the weighing errors due to air drafts. The power supply was capable of supplying amperages from 0.00 to 9.00 amps. These amperages corresponded to a magnetic field of from 000 to 12,000 gauss. Usually six readings, all at different magnetic fields, were recorded for each sample. All readings obtained when the sample tube appeared to be pulled to the poles of the magnet were omitted. The average deviation from the lowest force field to the highest was only about 0.05 Bohr Magnetons. The temperature was maintained at 299°K$\pm$1° for all readings. Corrections for diatomic atoms in each sample were made using Pascal's constants from the literature (42). None of the values recorded were corrected for temperature independent paramagnetism.

The nomenclature and procedure for obtaining the tube calibration constant at given force field strengths and the effective magnetic moments are given below.

A = weight of empty sample tube, zero current.

B = weight of empty sample tube, at a given current.

C = weight of filled sample tube, zero current.

D = weight of filled sample tube, at a given current.

α = 0.029 (the volume susceptibility of air) x volume of tube in cc.

S = B-A = apparent mass change for empty tube.

F = D-C = apparent mass change for filled tube.

F' = F-S = apparent mass change corrected for the diamagnetic character of the sample tube.

γ = temperature independent paramagnetism per metal ion.

β = tube calibration constant for a given field strength.

T = absolute temperature.

Calculation of "β" values using $Hg[Co(CNS)_4]$ as the standard:

$$\beta = \frac{16.44 \times 10^{-6} (C-A) - \alpha}{F'} \qquad (1)$$

Calculation of effective magnetic moments of samples:

$$\chi_g = \frac{\alpha + \beta F' (10^{-6})}{\text{sample weight}} \qquad (2)$$

$$\chi_{\text{molar}}^{\text{corrected}} = \chi_g (\text{molecular weight of the sample}) + \text{diamagnetic corrections.} \qquad (3)$$

$$\mu\text{eff.} = 2.84 \left[(\chi_{\text{molar}}^{\text{corrected}} - \gamma)\, T\right]^{1/2} \qquad (4)$$

A computer program to evaluate the susceptibilities and effective magnetic

moments is given in the appendix.

Molecular Weight and Association Studies

The molecular weight determinations and association values were obtained using a Mechrolab Model 301A Vapor Pressure Osmometer. For the low boiling solvents used in this study a 37° thermostat and probe were used. The instrument was allowed to "warm up" for at least twelve hours prior to the collection of any data. At the end of that time the "drift" of the needle due to a lack of equilibrium in the system was well within the tolerances specified by the manufacturer. Reagent grade chloroform and carbon tetrachloride without further purification were the solvents used. Standard curves were plotted with 0.0025 F, 0.0050 F, 0.0100 F, 0.0130 F, 0.0200 F, 0.0250 F, 0.0500 F and 0.1000 F solutions of diphenyl in chloroform and in carbon tetrachloride serving as the reference points. These two standard curves agreed well with other curves plotted from data obtained on the same instrument by other workers.

The four different concentrations of each unknown sample ranged from 0.0063 F to 0.1000 F. At least four different resistance readings for each sample concentration were recorded, and the averages of these formed the basis for molecular weight and association values at that particular concentration. For any given concentration, the variation of resistance values never exceeded three per cent and was usually much below one per cent.

It was found that two minutes was ample time for the system to return to equilibrium after another sample drop had been added to the thermistor bead. Time trials proved that the resistance readings for any one drop of sample did not vary from two minutes to one hour.

Spectral Studies

The infrared spectral data were collected with a Perkin-Elmer Model 21 Recording Infrared Spectrophotometer. The settings of the instrument were as follows:

Resolution	= 927	Suppression	= 4
Gain	= 5 1/2	Response	= 1
Speed	= 6		

A matched set of 0.10 mm sodium chloride cells were used. Both nujol mull spectra and chloroform solution spectra were run. All the infrared spectra were qualitative and no attempt was made to determine or record concentrations when chloroform solutions were used. A rerun of all the infrared spectra on a Perkin-Elmer Infracord Spectrophotometer gave identical absorption peaks although the resolution in the latter case was, of course, not as great. The 6.238 micron peak of polystyrene was the standard reference point in both cases.

The ultraviolet and visible spectra were obtained with a Cary Model 14 Recording Spectrophotometer. Again Fisher "Spectranalyzed" grade chloroform with no further purification served as the solvent. The matched cells were of 0.997 centimeter light path length. Sample solutions for the ultraviolet spectra were prepared by successive dilution of the sample solutions used for the visible spectra.

CHAPTER 4

RESULTS AND DISCUSSION

Potentiometric Titrations

Some important information concerning the formation of the methoxo derivatives of the divalent metal acetylacetonates can be obtained from the potentiometric titrations of the metal acetylacetonates with base. There is a distinct break in the curve which appears after the addition of one millimole of base to a sample of two millimoles of the complex. Table 9 and Figure 4 show the results of these titrations. The points on these curves simply represent values from the actual curves. The curve is consistent with the following two-step reaction.

$$\text{Step 1} \qquad 2\ MA_2 + CH_3O^- \rightleftharpoons [MAOCH_3\ (s)] + MA_3^- \qquad (1)$$

$$\text{Step 2} \qquad MA_3^- + CH_3O^- \rightleftharpoons [MAOCH_3\ (s)] + 2\ A^- \qquad (2)$$

Although both steps essentially involve the replacement of an acetylacetonate group by a methoxide ion, the stability due to chelation is retained in Step 1 by the chelation of the replaced acetylacetonate group to a MA_2 molecule to form MA_3^-; however, in Step 2, two chelate rings must be destroyed to reach the observed product. Equilibrium in Step 1, thus, would be expected to lie much further to the right than the equilibrium in Step 2. This is in agreement with observations.

Table 9. Potentiometric Readings for Titration of 2.00 mm of MA_2 versus KOH Relative pH of Solutions.

mm.KOH	Co	Ni	Mg
0.00	6.00	6.00	6.00
0.05	6.10	6.55	----
0.10	6.20	6.81	7.80
0.15	6.38	6.85	----
0.20	6.56	6.88	8.50
0.30	7.42	6.92	8.80
0.40	7.55	7.05	8.86
0.50	7.60	7.10	9.03
0.60	7.70	7.20	9.15
0.70	7.75	7.32	9.20
0.80	7.83	7.50	9.30
0.85	7.91	7.61	----
0.90	8.00	7.72	9.37
0.95	8.40	7.90	----
1.00	8.80	8.11	----
1.05	9.20	8.45	9.40
1.10	9.60	8.98	9.42
1.20	9.90	9.75	9.45
1.25	10.20	10.00	----
1.40	10.40	10.28	9.47
1.60	10.60	10.45	9.49
1.80	10.71	10.55	9.50
2.00	10.76	10.58	9.52

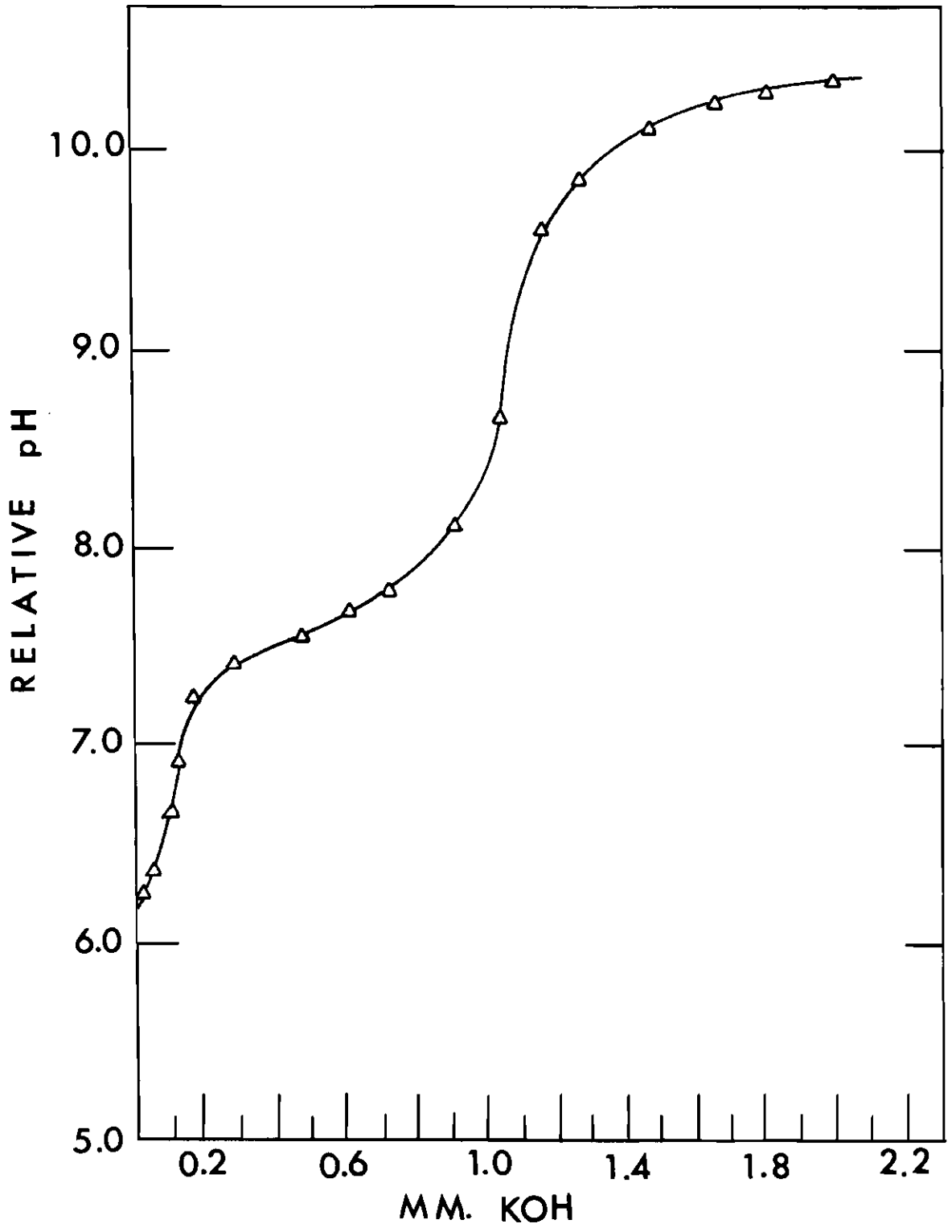


Figure 4. The Titration of 2.00 mm CoA_2 versus KOH

Existence of a MA_3^- specie is known from other work. Figgis and Nyholm (4) have conducted magnetic studies on the complex, $K[CoA_3]$, while Cotton and Soderberg (43) have made spectral studies of the same complex.

To test the validity of the proposed reactions, all of the MA_2 was converted to the MA_3^- before the titrations were begun. This was accomplished by the addition of equimolar amounts of MA_2 and an alkali metal acetylacetonate such as potassium acetylacetonate. When a solution of this type employing 2.00 mm of CoA_2 and 2.00 mm of KA was titrated with KOH, the curve shown in Figure 5 was obtained. The absence of a break clearly indicates that Step 1 of the reaction has been suppressed and that only Step 2 is occurring.

Reaction with the base does occur, however, since $CoA(CH_3O)(CH_3OH)$ is precipitated as the base is added. The occurrence of Step 2 is also evident in the preparation of these complexes since Step 1 could only yield 50 per cent of the product and the actual yields approach 100 per cent.

The reversibility of these reactions was of interest since this point had been questioned. The reverse titrations were complicated by the precipitation of the methoxo complexes in the isopropyl alcohol used as solvent. However, with high speed stirring and a time lapse long enough to insure complete reaction with the HCl, the reactions did prove to be reversible. The hysteresis effect noted earlier was completely eliminated, and the curve of MA_2 versus KOH was retraced almost exactly by the reverse titration with HCl.

The equilibria discussed above are complicated by the relative

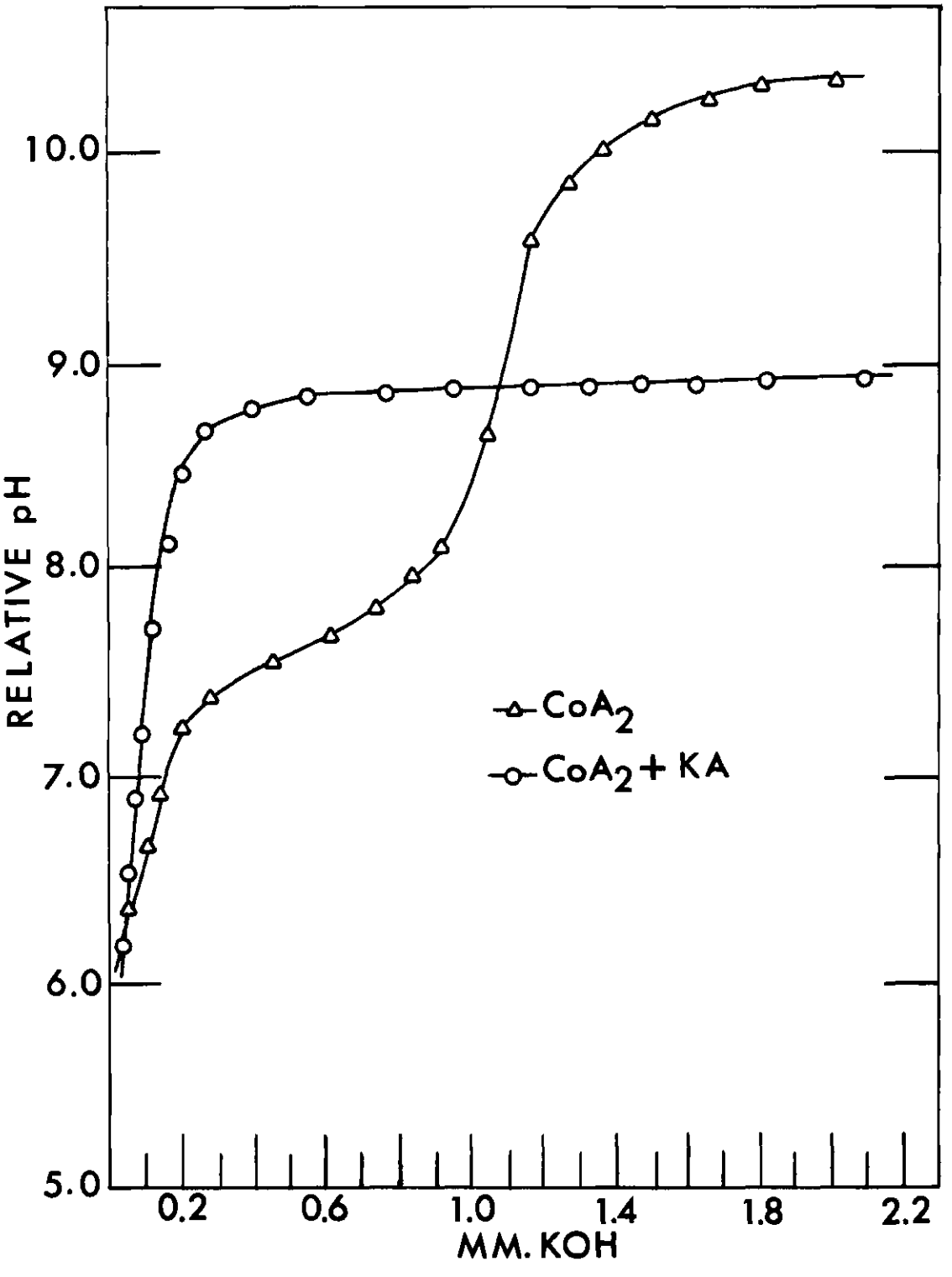


Figure 5. Comparison of the Titration of 2.00 mm Co_2 versus KOH and the Titration of 2.00 mm CoA_2 plus 2.00 mm KA versus KOH.

stabilities of MA_2 and MA_3^- complexes and by the solubility of the product, $MA(CH_3O)(CH_3OH)_x$. A simpler system is necessary to obtain information about the relative stabilities of the complexes of different metal ions.

Titration of the methoxo complexes with HCl produced the curves shown in Figure 6. In all cases 0.80 millimoles of the complex was titrated. It should be pointed out here that due to the limited amount of acetylacetone present in these titrations (one acetylacetone per metal ion) these reactions are <u>not</u> the reverse of the reactions of MA_2 with base where there are two acetylacetones per metal ion.

The $CuA(CH_3O)$ curve has two distinct breaks, one occurring at about 0.85 millimoles of KOH added representing the titration of the methoxide portion of the complex, and one occurring at about 1.60 millimoles of base added representing the titration of the acetylacetone portion. The following two-step procedure may be used to explain the curve.

$$\text{Step 1} \quad MA(CH_3O) + H^+ \rightleftharpoons MA^+ + CH_3OH \tag{3}$$

$$\text{Step 2} \quad MA^+ + H^+ \rightleftharpoons M^{++} + HA \tag{4}$$

Many workers including Celiano, et al. (41), Van Uitert, et al. (40), and Calvin, et al. (39) have presumed the existence of the cationic specie, MA^+.

The $CoA(CH_3O)(CH_3OH)$ shows a behavior similar to that of the copper complex. One break at 2.10 millimoles of the base is distinct, but the break at about 1.10 millimoles of KOH is not as clearly discernable.

Table 10. Potentiometric Readings for Forward Titration of 0.80 mm. of $MA(CH_3O)(CH_3OH)_x$ versus HCl.

	Millivolts			
mm.HCl	Co	Ni	Cu	Mg
0.00	-389	-258	-278	-445
0.12	-316	-216	-269	-429
0.24	-348	-189	-253	-411
0.36	-339	-174	-228	-380
0.48	-321	-157	-200	-356
0.60	-309	-132	-176	-329
0.71	-285	-113	-147	-308
0.83	-254	-091	-100	-280
0.95	-223	-084	-016	-270
1.07	-200	-071	032	-250
1.19	-177	-043	062	-221
1.31	-155	000	084	-200
1.43	-130	050	111	-180
1.55	-110	116	139	-160
1.67	-097	186	194	-138
1.79	-073	216	222	-115
1.90	-029	230	231	-088
2.02	----	235	243	-055
2.14	172	238	251	131
2.26	215	245	257	18s
2.38	238	251	263	210

Table 10. (Continued)

mm.HCl	Co	Ni	Cu	Mg
2.50	250	258	267	225
2.62	261	264	270	240
2.74	272	270	278	----

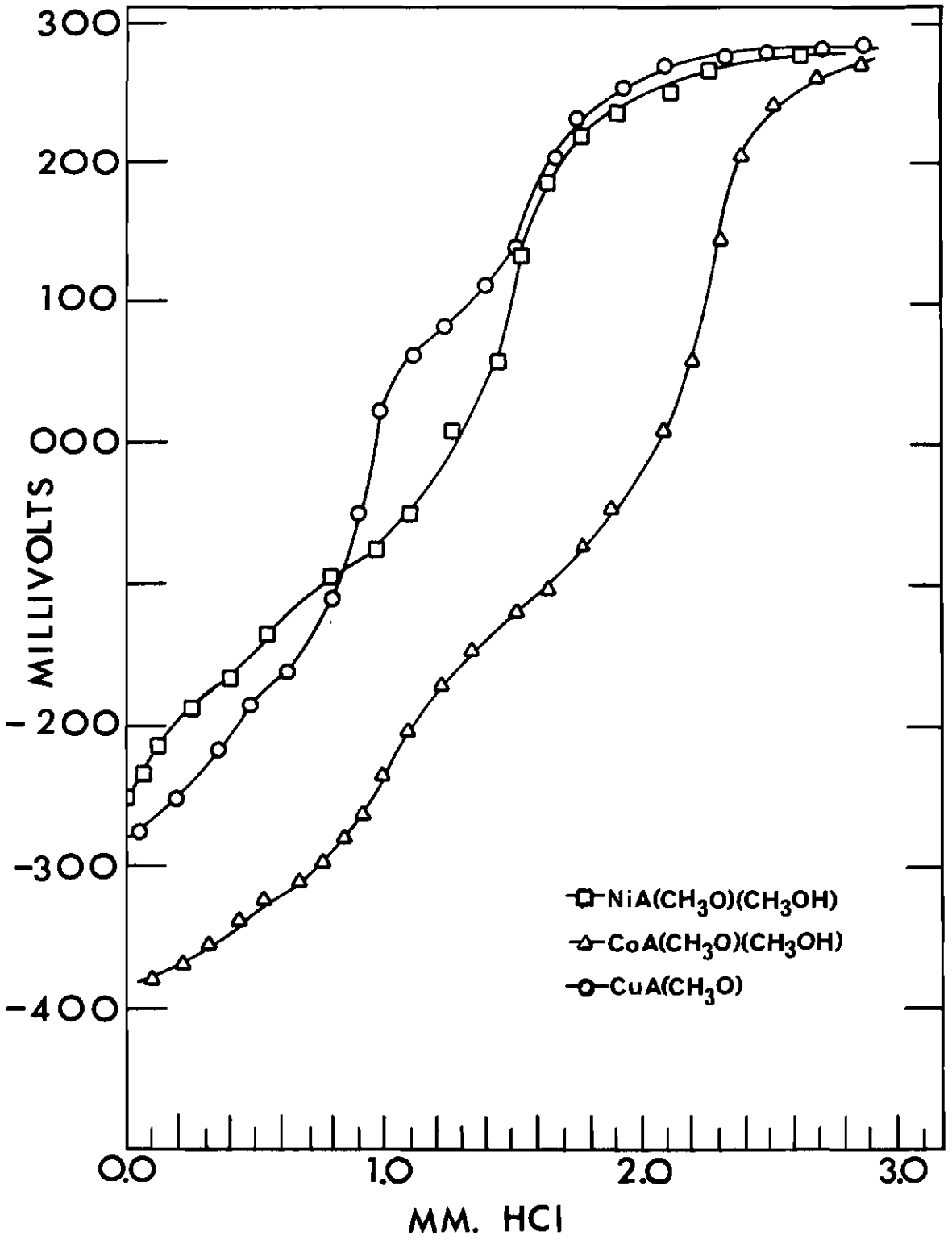


Figure 6. Titration of 0.80 mm $MA(CH_3O)(CH_3OH)_x$ versus HCl

The behavior of the $NiA(CH_3O)(CH_3OH)$ is different from that of the cobalt and the copper complexes since only one break is clearly discernible in the titration. This indicates that the two equilibrium constants, K_1 and K_2, are not sufficiently different, in the case of nickel, to give independent steps in the reaction. In the cobalt and copper cases these constants are sufficiently different to yield two definite breaks.

Van Uitert, Fernelius, and Douglas (44) reported that the stabilities of the diketones of the above mentioned metals were in this order of stability: Cu > Ni > Co > Mg. The methoxo derivatives seem to show the same order of stability. From Figure 6, it can be seen that the cobalt curve falls below the nickel curve at all points. This is to be expected since the cobalt complex is more weakly coordinated than the nickel complex and thus is a stronger base toward HCl. The cross-over of the copper and nickel curves is probably a result of different coordination and/or different bonding in the two complexes since different coordination for the two complexes is also suggested by their different formulas. However, a strict comparison of the two curves is not possible.

The apparent shift of the cobalt curve to the right is not fully understood. One possible explanation is that the complex readily loses its methanol of solvation, and what was thought to be only 0.80 millimoles of the complex was, in essence, more. The extra amount of complex required more acid to titrate it.

The reverse titrations using KOH did not entail the same difficulties of insolubility as the titrations of the metal acetylacetonates with KOH had. In no case was a precipitate observed. Figure 7, using

$CuA(CH_3O)$ as an exemplary example, shows that this type titration was completely reversible.

Table 11. Potentiometric Readings for the Reverse Titration of 0.80 mm $MA(CH_3O)(CH_3OH)_x$ versus KOH

mm KOH	Millivolts Co	Ni	Cu	Mg
0.00	273	270	278	240
0.10	270	265	274	238
0.20	268	258	270	235
0.30	266	253	267	230
0.40	264	244	263	220
0.50	260	240	260	170
0.60	252	236	258	080
0.70	246	220	254	050
0.80	228	200	248	030
0.90	162	187	245	005
1.00	062	180	240	-010
1.10	----	165	236	----
1.20	-050	108	228	-102
1.30	-059	041	206	-112
1.40	-070	003	198	-127
1.50	-083	-032	142	-139
1.60	-100	-054	119	-153
1.70	-118	-081	089	-172

Table 11. (Continued)

mm KOH	Millivolts Co	Ni	Cu	Mg
1.80	-140	-098	078	-190
1.90	-167	-105	073	-219
2.00	-200	-113	031	-240
2.10	-214	-124	-071	-254
2.20	-223	-148	-088	-271
2.30	-232	-163	-115	----
2.40	-241	-174	-150	-301

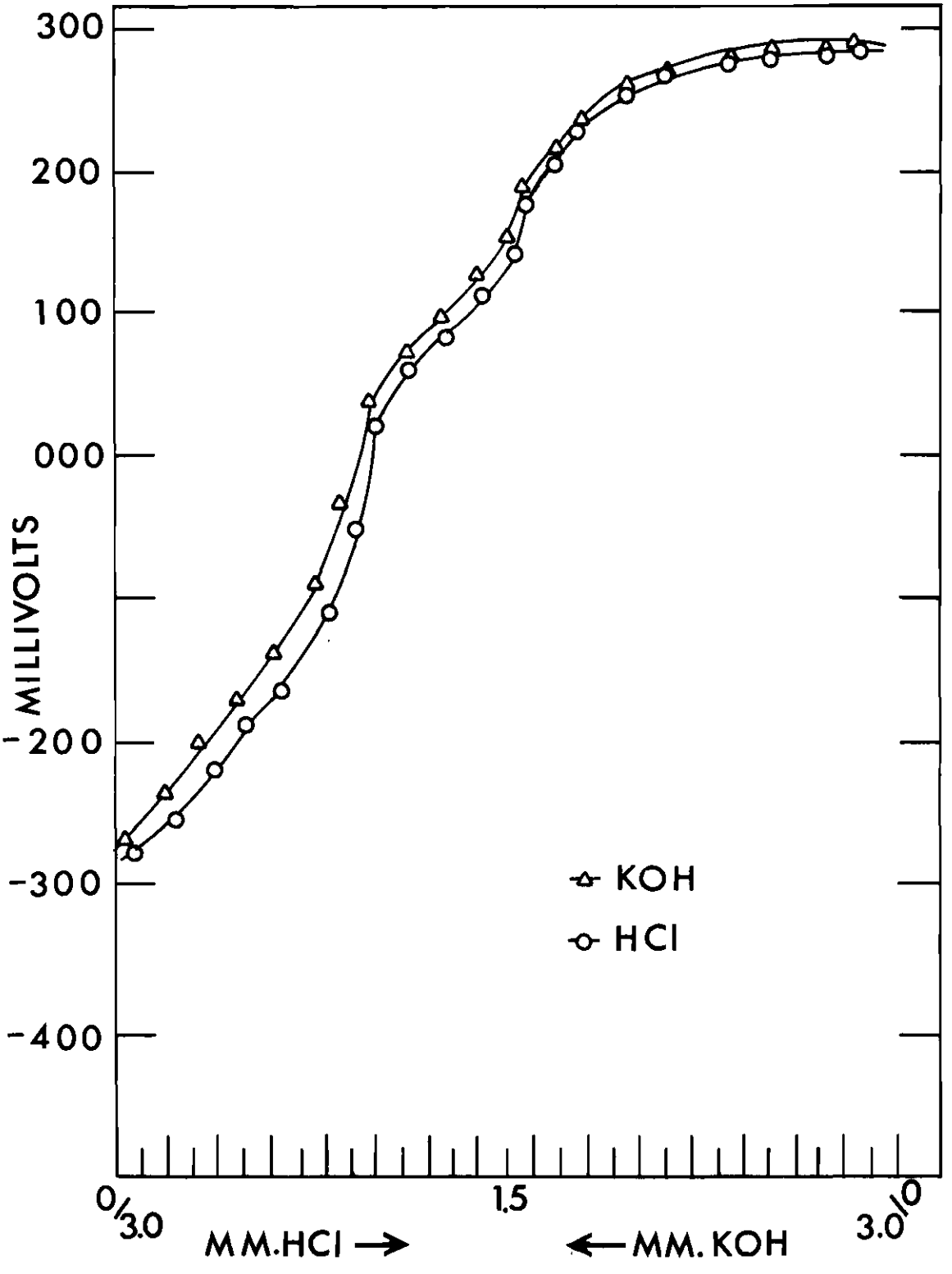


Figure 7. Forward and Reverse Potentiometric Titrations of 0.80 mm $CuA(CH_3O)(CH_3OH)$.

Magnetic Studies of the Methoxo Complexes

The results of the magnetic studies of the magnesium, nickel, cobalt, and copper complexes are summarized in Table 12. There are several features of the magnetic properties which merit attention. As would be expected, the magnesium complex is diamagnetic for all magnetic field strengths. The nickel complex exhibits a moment well within the range expected for an octahedrally surrounded nickel with two unpaired electrons. Similarly, the cobalt complex shows a normal moment for a spin-free octahedral complex.

When the methanol of solvation of the cobalt complex is removed by drying in a drying pistol for three hours over benzene, magnetic moments were lower by about one-tenth of a Bohr Magneton. This reduction of the magnetic moment is too slight to indicate a change in complex coordination.

The copper complex is perhaps the most interesting for it shows a magnetic moment considerably below the spin-only value of 1.73 B.M. normally anticipated. It was virtually impossible to determine if the subnormal value arises from a direct copper-copper interaction or from superexchange, without the aid of a structure determination. This complex will be discussed in further detail when its molecular association and spectra are discussed.

Table 12. Magnetic Data for the Methoxo Complexes

Complex	Power Supply Amperage	$\chi^{Corrected}_{Molar} \times 10^6$	μeff., B.M.
$NiA(CH_3O)(CH_3OH)$	3.0	4935.7	3.45
	5.0	4983.2	3.47
	8.0	4753.0	3.39
$MgA(CH_3O)(CH_3OH)$	1.5		
	2.0		
	3.0	All Diamagnetic	
	5.0		
	7.0		
$CuA(CH_3O)^{*,**}$	3.0	264.87	0.80
	4.0	283.45	0.83
	5.0	279.58	0.82
	6.0	289.26	0.84
	7.0	220.36 295.06	0.77 0.84
	8.0	249.58 298.94	0.78 0.85
	9.0	235.46 300.87	0.77 0.85
$CoA(CH_3O)(CH_3OH)$	2.0	11,027.3	5.16
	2.5	10,855.7	5.12
	3.0	10,360.2	5.01
	3.5	11,253.4	5.21
	4.0	10,543.5	5.02
	4.5	11,060.4	5.17

Table 12. (Continued)

Complex	Power Supply Amperage	$\chi^{Corrected}_{Molar} \times 10^6$	μeff., B.M.
$CoA(CH_3O)$	2.0	9,966.3	4.90
	3.0	9,518.6	4.81
	4.0	10,004.6	4.91
	5.0	10,023.4	4.91
$CuSal(CH_3O)$	4.0	777.4	1.37
	5.0	824.1	1.41
	6.0	827.8	1.41
	7.0	772.4	1.36
	8.0	811.2	1.40
	9.0	825.9	1.41

Note: * -- Not corrected for temperature independent paramagnetism.

** -- More than one value represent readings taken with different balances.

Molecular Weights and Associations of the Methoxo Complexes

Table 13 contains a summary of the data obtained by osmometry on the molecular weights and associations of the methoxo complexes in chloroform. In all osmometry data, an error of about five per cent may be expected. Since all of the complexes show association in solution, bridging groups are indicated; however, since both the methoxide ion and the acetylacetonate ion are known to form bridges in various compounds, molecular weight data alone is not sufficient to determine the molecular structures.

The nickel, magnesium, and cobalt compounds show associations of between four and eight. Although the individual values may be meaningful in terms of the solid state structures, it seems more likely that in the solid state all of these are present as infinite polymers, and that the particular values obtained in solution are a result of the tendency of the metal ion to maintain an octahedral coordination.

For the magnesium and cobalt complexes molecular association shows a decrease on dilution as expected for such systems. The opposite effect in the case of the nickel complex is probably not real but the result of experimental errors.

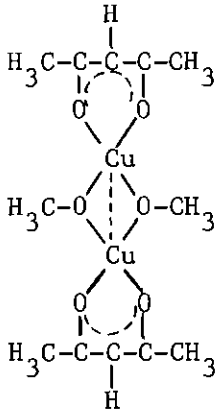
The copper complex shows an association of two which is constant on dilution. This property coupled with the low magnetic moment and the tendency for copper(II) to achieve four-coordination strongly suggest that bridging groups are present. Although copper(II) acetylacetonate has no bridging oxygens, this does not exclude the possibility of their existence in the methoxo complex. However, the methoxide ion often acts as a bridging group in such compounds as copper(II) methoxide (45), and

Table 13. Molecular Weights and Associations*

Complex	Solvent	Concentration	Mol. Weight	Association
$NiA(CH_3O)(CH_3OH)$	$CHCl_3$	0.0250 F	975	4.5
		0.0500 F	840	3.8
		0.1000 F	789	3.6
$MgA(CH_3O)(CH_3OH)$	$CHCl_3$	0.0250 F	931	5.0
			932	5.0
		0.0500 F	932	5.0
			849	4.5
		0.1000 F	1242	6.6
$CuA(CH_3O)$	$CHCl_3$	0.0250 F	439	2.2
		0.0500 F	403	2.1
			350	1.8
			395	2.0
$CoA(CH_3O)(CH_3OH)$	$CHCl_3$	0.0250 F	1147	5.2
		0.0500 F	1410	6.4
		0.1000 F	1760	7.7
$CoA(CH_3O)$	$CHCl_3$	0.0125 F	875	4.6
		0.0250 F	1004	5.3
		0.0500 F	1180	6.2
		0.1000 F	1362	7.2

Note: * -- More than one value for a given concentration represent data for different samples on different days.

this seems to be a more probable structure. A likely structure for the copper methoxo complex is the one shown below.



Spectra of the Methoxo Complexes

I. Infrared Spectra. Table 14 gives the values for the absorption bands of the methoxoacetylacetonates in chloroform. The absorption bands between 1600 cm^{-1} and 650 cm^{-1} of the parent acetylacetonates are also given for comparison. All the parent compounds were run using the KBr disc method except the magnesium acetylacetonate which was run in chloroform solution. The methoxo complexes' absorption peaks below 800 cm^{-1} were not recorded.

There are several interesting features which should be noted in a comparison of the spectra.

(1) Whereas the MA_2 spectra have somewhat broad absorption bands, the $MA(CH_3O)(CH_3OH)_x$ absorptions are very sharp. This is especially noticeable in the carbonyl stretching region. Since there are two acetylacetonate rings in each of the parent compounds, the absorptions are due to a contribution from each ring. The methoxo derivatives, on

Table 14. Infrared Absorption Bands for Metal Chelates (cm^{-1})

Copper(II)		Nickel(II)		Cobalt(II)		Magnesium(II)	
A*	MeA**	A	MeA	A	MeA	A	MeA
----	----	----	3275	----	3325	----	3250
----	----	----	2940	----	2970	----	2960
----	----	----	2825	----	2810	----	2840
1580	1590	1598	1612	1601	1609	1614	1620
1554							
1534	1533	1514	1522	1513	1524	1522	1522
1464	1460	1453	1453	1461	1455	1469	1467
1415	1397	1398	1408	1398	1410	1413	1412
1356		1367	1368	1366	1367	1368	1368
			1310				
1274	1280	1261	1260	1261	1262	1264	1263
1190		1198		1199	1187		1195
			1090				
	1055(v.wk.)		1053(v.st.)		1046(v.wk.)		1062
1020	1020	1020	1018	1020	1018	1017	(v.wk.) 1020
937	936	929	923	931	923	923	924
781		764		767			
684		666		672			
654				659			

Note: * -- Acetylacetonate ** -- Methoxyacetylacetonate

the other hand, have only one ring, and this single contribution accounts for the sharpness of the bands.

(2) All of the methoxo complexes show an absorption peak between 1062 cm^{-1} and 1045 cm^{-1} which is absent in their parent complexes. It has been suggested (46) that this region corresponds to a carbon-oxygen stretching of terminal methoxides. This peak is very weak in all of the complexes except the nickel case in comparison to the 1020 cm^{-1} peak found in the parent complexes as well as in the derivatives. The region below 1040 cm^{-1} is also the region for absorption by bridging methoxides. The behavior exhibited by the nickel complex is indicative of both bridging and terminal methoxides, whereas the other methoxo complexes show absorption for only bridging methoxides. However, overlapping of absorption zones in the 1020 cm^{-1} region make it impossible to <u>definitely</u> state that bridging methoxides are present.

II. <u>Ultraviolet Spectra</u>. The ultraviolet spectra of the methoxo complexes and their corresponding parent acetylacetonates are contained in Table 15. The methoxo complexes show broad absorption bands with their maxima centered around the wavelengths given. Absorptions for these complexes are identical to those of the acetylacetonates in position, but the intensities vary. The intensities in the methoxo complexes are approximately one-half those of the parent compounds since one of the acetylacetonate rings has been replaced. Figure 8 shows a comparison of the ultraviolet spectra of copper acetylacetonate and its methoxo derivative. The similarities are evident. There appears to be no significant change of bonding when the acetylacetonates are converted to their corresponding methoxo derivatives. The acetylacetonate rings are in the

monoanionic form in both classes of compounds.

Table 15. Ultraviolet Absorption Bands for Metal Chelates

Metal	Solvent	λmax. Acetylacetonate		Methoxoacetylacetonate	
		cm^{-1}	mμ	cm^{-1}	mμ
Cu	$CHCl_3$	40,800	245	41,200	243
		33,800	296	33,800	296
Ni	$CHCl_3$	37,700	265	------	---
		33,800	296	32,900	304
Co	$CHCl_3$	34,200	292	33,800	296
Mg	$CHCl_3$	35,200	284	34,400	291

III. Visible Spectra. The visible spectra are summarized in tabular form in Table 16. The cobalt and nickel complexes show the spectra normally expected for octahedrally coordinated compounds. For example, the molar extinction coefficient of the cobalt complex is approximately 19.0 and its maximum absorption around 20,000 cm^{-1}. Tetrahedral cobalt shows molar extinction coefficients of about 200 and maxima centered around 16,500 cm^{-1}.

The copper methoxo complex whose visible spectrum is shown in Figure 9 is similar in intensity and position to that of the bis acetylacetonato complex and other known square planar complexes of copper(II). Tetrahedral complexes of copper(II) with oxygen donors do not absorb in the visible region, the weaker crystal field causing a shift to lower

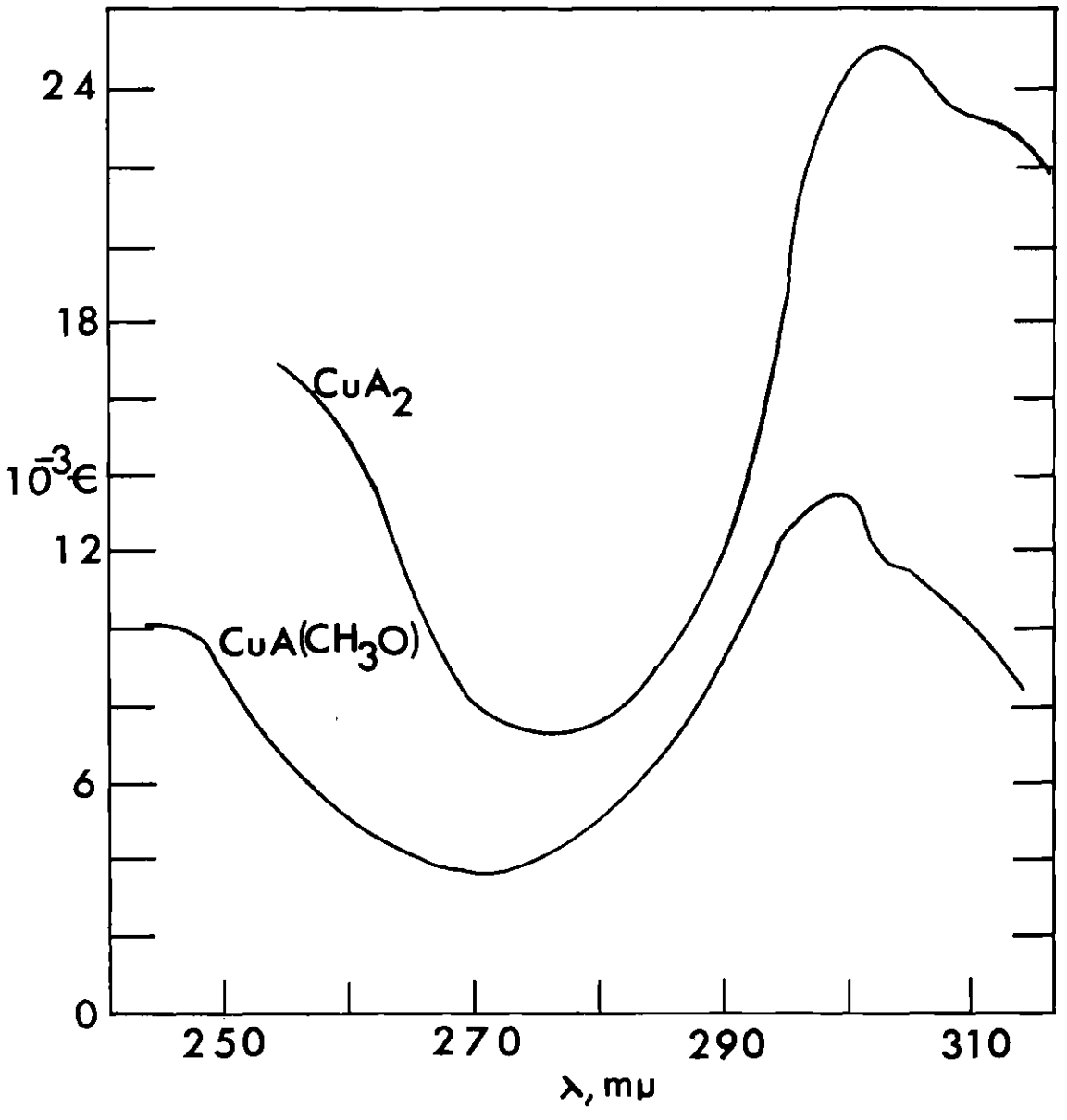


Figure 8. Ultraviolet Spectra of Di-μ-methoxobis(2,4-pentanediono) di-copper(II) and Bis(2,4-pentanediono)copper(II). Extinction coefficients are based on formular weight per copper(II) ion.

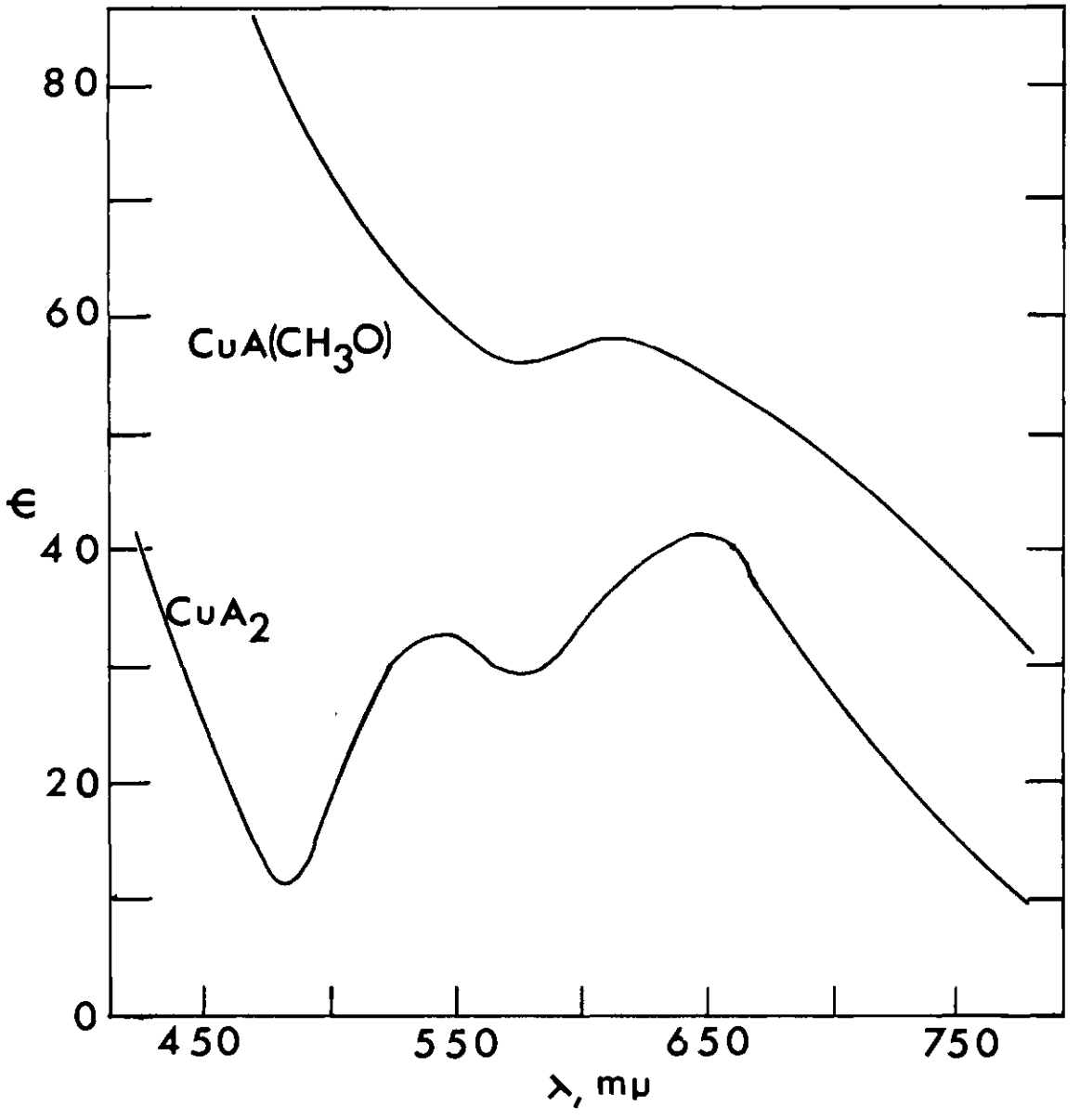


Figure 9. Visible Spectra of Di-μ-methoxobis(2,4-pentanediono)di-copper(II) and Bis(2,4-pentanediono)copper(II). Extinction coefficients are based on formula weight per copper(II) ion.

energy (47).

Table 16. Visible Absorption Maxima for Metal Chelates

Metal	Solvent	λ_{max}. Acetylacetonate		Methoxoacetylacetonate	
		cm^{-1}	mμ	cm^{-1}	mμ
Cu	$CHCl_3$	18,500	541	------	---
		15,900	629	15,800	633
Ni	$CHCl_3$	15,100	662	15,400	649
Co	$CHCl_3$	20,000	500	20,100 (sh.)	498
				19,050	525

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

This has been the first work performed on the methoxo derivatives of the first row transition element acetylacetonates, although similar methoxo derivatives of non-transition metal acetylacetonates have already been prepared and studied.

This work, through the use of potentiometric titrations, has elucidated the step-wise processes by which the parent acetylacetonates are converted into their corresponding methoxo derivatives. The magnetic moment and spectral studies have helped suggest plausible structures for the methoxo complexes. All of the transition metal complexes appear to be octahedrally coordinated, except the copper complex which is square-planar. Molecular weight studies of these complexes in solution have shown that while some of the complexes show definite stability at certain association values, others show decreased association upon dilution. The existence of bridging methoxide groups has been confirmed.

Many allied problems have arisen since the work was originally started. Some of the following problems have been and are being investigated in these laboratories.

(1) A single crystal X-ray structure determination of the $CoA(CH_3O)(CH_3OH)$ complex has been started. It is hoped that knowledge of the structure of this complex will enable us to understand more about the bonding in such complexes.

(2) The effects of various substituents on the acetylacetonate

rings of the methoxo complexes will be studied. These substituents could possibly affect the stability, bonding, association, and magnetic character of such complexes.

(3) Since there seem to be serious discrepancies in the current chemical literature concerning the properties and characterization of copper(II)hexafluoroacetylacetonate and its adducts, work has now been completed on the properties of the anhydrous, monomethanolate, and dihydrate of the complex. Since this work did not seem to fit in the text of the thesis, it was omitted but it will appear later in the literature.

(4) The use of "bridging groups" other than the methoxide ion could possibly yield significant information about the effect of various bridging agents and metal-metal interaction in such complexes.

APPENDIX

COMPUTER PROGRAM FOR CALCULATION OF GRAM SUSCEPTIBILITIES, MOLAR SUSCEPTIBILITIES, AND EFFECTIVE MAGNETIC MOMENTS*

The following program was written in modified ALGOL language especially for the Burroughs B-5500 computer.

Definitions of Symbols

A = Weight of empty tube, zero current

C = Weight of tube plus standard, zero current

G = Weight of tube plus sample, zero current

V = Volume of tube in cubic centimeters

K = Constant for standard used

Amp= Amperage of power supply

B = Weight of empty tube, given magnetic field

D = Weight of tube plus standard, given magnetic field

X = Weight of tube plus sample, given magnetic field

S, E, F, Beta, XG, XM, XC CORR, MUF are defined in the program.

---

*We wish to thank Mr. D.L. Plymale for writing this program.

```
BEGIN
COMMENT MAGNETIC SUSCEPTIBILITY PROGRAM                                ;
REAL PASCA, MOLW, TEMP, A,C, G, V, K, AMP, B, D, X, S, E,
F, BETA, XG, XM, XC  CORR, MUF                                         ;
INTEGER I                                                              ;
ALPHA ARRAY  NA[1:12]                                                  ;
LABEL LOOP, TOP, BOTTOM                                                ;
FILE IN F 1  (2, 10)                                                   ;
FILE OUT F 2 1(2, 15)                                                  ;
FORMAT TITLE  (12A6)                                                   ;
FORMAT IN FORMI  (X3, 3F9.3)                                           ;
FORMAT IN FORM2  (X5, 5F9.6)                                           ;
FORMAT IN FORM3  (X5, 4F9.6)                                           ;
FORMAT OUT FORM4  (X6,"AMP", X8, "BETA", X8"TEMP", X9, "XG", X10,
"XC", X10, "MUF" )                                                     ;
FORMAT OUT FORM5  (6F12.4)                                             ;

TOP:
READ  (F1, FORM1, PASCA, MOLW, TEMP)                                   ;
IF PASCA = 0 THEN GO TO BOTTOM                                         ;
READ  (F1, FORM2, A, C, G, V, K)                                       ;
READ  (F1, TITLE, FOR I←1  STEP 1 UNTIL 12 DO NA[1])                   ;
WRITE F2[DBL], TITLE, FOR I←1  STEP 1 UNTIL 12 DO NA[I])               ;
WRITE (F2[DBL], FORM4)                                                 ;
LOOP:
READ  (F1, FORM3, AMP, B, D, X)                                        ;
```

```
IF AMP ≠ 0 THEN BEGIN
   S←B - A                                                    ;
   E←(D - C - S) x 1000                                       ;
   F←(X - G - S) x 1000                                       ;
BETA←(K x (C - A) - (0.029) x V) / E                          ;
   XG←((0.029) x V + BETA x F) / (G - A)                      ;
XM←XG x MOLW                                                  ;
XC←XM + PASCA                                                 ;
CORR←SQRT (XC x TEMP)                                         ;
MUF←(2.84) x CORR x 0.001                                     ;
WRITE  (F2, FORM5, AMP, BETA, TEMP, XG, XC, MUF)              ;
GO TO LOOP                                                    ;
END                                                           ;
GO TO TOP                                                     ;
BOTTOM:
END.
```

LITERATURE CITED

1. B.N. Figgis, Nature, 182, 1568 (1958).

2. H.J. Van Vleck, Theory of Electric and Magnetic Susceptibilities, Oxford University Press, London, (1932), pp. 286.

3. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, A Comprehensive Text, Interscience Publishers, New York, N. Y., (1962), pp. 736.

4. B.N. Figgis and R.S. Nyholm, Journal of the Chemical Society, I, 338 (1959).

5. Harris and Stevenson, unpublished work.

6. F.A. Cotton and J.P. Fackler, Jr., Journal of the American Chemical Society, 83, 2818 (1961).

7. J. Lifschitz and E. Rosenbohm, Journal of Electrochemistry, 21, 499, (1915).

8. M. Kato, H.B. Jonassen, and J.C. Fanning, Chemical Reviews, 64, no. 2, 99 (1964).

9. J.N. van Niekerk, and F.R.L. Schoening, Acta Crystallographica, 6, 227 (1953).

10. H.L. Schafer, J.C. Morrow, and H.M. Smith, Journal of Chemical Physics, 42, 504 (1965).

11. E.G. Cox, and K.C. Webster, Journal of the Chemical Society, 731 (1935).

12. H. Koyama, Y. Saito, and H. Kuroya, Journal of Institute of Polytechnics, Osaka, 4C, 43 (1953).

13. L.F. Dahl, 1961, unpublished work.

14. F.A. Cotton and R.H. Soderberg, Inorganic Chemistry, 3, 1 (1964).

15. F.A. Cotton and R.C. Elder, Journal of the American Chemical Society, 86, 2294 (1964).

16. S. Shibata, Bulletin of the Chemical Society, Japan, 30, 842 (1957).

17. S. Shibata, Bulletin of the Chemical Society, Japan, 30, 753 (1957).

18. J.P. Fackler, Jr., and F.A. Cotton, Journal of the American Chemical Society, 83, 3775 (1961).

19. G.J. Bullen, R. Mason, and P. Pauling, Nature, 189, 291 (1961).

20. G.J. Bullen, Nature, 177, 537 (1956).

21. D.C. Bradley, Progress in Inorganic Chemistry, Volume 2, Interscience, New York, N.Y., (1960), pp. 337.

22. R.A.D. Wentworth and C.H. Brubaker, Jr., Inorganic Chemistry, 3, 47 (1964).

23. R.M. Klein and J.C. Bailar, Jr., Inorganic Chemistry, 2, 1187 (1963).

24. R.L. Belford, A.E. Martell, and M. Calvin, Journal of Inorganic and Nuclear Chemistry, 2, 11 (1956).

25. H.F. Holtzclaw and J.P. Collman, Journal of the American Chemical Society, 79, 3318 (1957).

26. K. Ueno and A.E. Martell, Journal of Physical Chemistry, 59, 998 (1955).

27. J. Lecompte, Discussions of the Faraday Society, 9, 125 (1950).

28. K. Nakamoto, Y. Morimoto, and A.E. Martell, Journal of Physical Chemistry, 66, 346 (1962).

29. R.H. Holm and F.A. Cotton, Journal of the American Chemical Society, 80, 5658 (1958).

30. F.A. Matsen, Technique of Organic Chemistry, Volume IX, Interscience, New York, N. Y., (1963), pp. 686.

31. R.M. Izatt, W.C. Fernelius, and B.P. Block, Journal of Physical Chemistry, 59, 80 (1955).

32. C.K. Jørgensen, Acta Chemica Scandinavica, 9, 116 (1955).

33. C.J. Ballhausen and C.K. Jørgensen, Acta Chemica Scandinavica, 9, 397 (1955).

34. O.G. Holmes and D.S. McClure, Journal of Physical Chemistry, 26, 1686 (1957).

35. C.J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill Book Company, Inc., New York, N. Y., (1962), pp. 261.

36. C.K. Jørgensen, Acta Chemica Scandinavica, 9, 1362 (1955).

37. W.C. Fernelius and B.E. Bryant, Inorganic Syntheses, Volume 5, 105 (1957).

38. J.A. Bertrand and D. Caine, Journal of the American Chemical Society, 86, 2298 (1964).

39. M. Calvin and K.W. Wilson, Journal of the American Chemical Society, 67, 2003 (1945).

40. L.G. van Uitert and C.G. Haas, Journal of the American Chemical Society, 75, 451 (1953).

41. A.V. Celiano, M. Cefola, and P.S. Gentile, Journal of Physical Chemistry, 65, 2194 (1961).

42. J. Lewis and R.G. Wilkins, Modern Coordination Chemistry, Principles and Methods, Interscience Publishers, Inc., New York, N. Y., (1960), pp. 403.

43. F.A. Cotton and R.H. Soderberg, unpublished work.

44. L.G. van Uitert, W.C. Fernelius, and B.E. Douglas, Journal of the American Chemical Society, 75, 2736 (1953).

45. C.H. Brubaker, Jr., and M. Wicholas, Journal of Inorganic and Nuclear Chemistry, 27, 59 (1965).

46. C.G. Barraclough, D.C. Bradley, J. Lewis, and I.M. Thomas, Journal of the Chemical Society, 2601 (1961).

47. Ballhausen, reference 35, pp. 272.